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The Effects of Organic Adsorbates on the Underpotential and Bulk
Deposition of Silver on Polycrystalline Platinum Electrodes

S.H. Harford, D.L. Taylor, and H.D. Abruña
Department of Chemistry
Baker Laboratory
Cornell University
Ithaca, New York 14853-1301

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The Effects of Organic Adsorbates on the Underpotential and Bulk Deposition of Silver on Polycrystalline Platinum Electrodes

S.H. Harford, D.L. Taylor, and H.D. Abruña*

Department of Chemistry, Baker Laboratory

Cornell University, Ithaca, NY 14853-1301

Abstract

The effects of various heterocyclic co-adsorbates (pyridine, pyrazine, 2,2'-bipyridyl, 4,4'-bipyridyl, 4-phenylpyridine, 4-mercaptopyridine, and 2-mercaptopyridine) on the electrodeposition of silver onto polycrystalline platinum electrodes in 0.10M H₂SO₄ have been studied using cyclic voltammetry. Adsorbates bonding through a nitrogen hetero-atom significantly hinder both the silver underpotential (UPD) and bulk deposition processes. The existence of a Pt/Ag/adsorbate structure is proposed based on the significant overpotential necessary to initiate bulk deposition. The sulfur-containing heterocycles completely inhibit silver UPD as well as the formation of a PtO film on the polycrystalline electrode. The only observable processes were bulk deposition (at overpotentials on the order of 125mV) and subsequent bulk stripping of silver. The effects of having a polycrystalline surface have been assessed by comparing these results to those from studies of silver deposition onto Pt(111) surfaces in the presence of the same co-adsorbed species.

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Introduction

The electrodeposition of silver onto polycrystalline platinum electrodes has been the subject of numerous investigations [1-8]. Initial studies by Cadle and Bruckenstein [1] characterized the inhibitive effects of silver deposition on the adsorption of hydrogen and they determined that an amount equivalent to 1.4 monolayers was necessary to completely block the surface. More recent investigations have focused on Ag/Pt alloy formation, kinetic controls to deposition, nucleation and growth models of adatom layers, and competitive adsorption between silver and oxygen [2-8]. Studies by Szabo [2,3] and Chierchie [4] have addressed some of the effects of platinum oxide coverage on silver UPD. Scharifker has investigated the possibility of alloy formation [5], and Arvíá has proposed the existence of energetically distinct silver layers deposited at underpotentials [6-8].

The presence of co-adsorbates has been shown to have a pronounced effect on the voltammetric behavior of silver and copper deposition onto foreign metal substrates, especially in the underpotential region. Several groups have shown that the presence of halides and pseudo halides significantly alters the deposition mechanism of metal monolayers on Pt (111) electrodes [9-16]. Using electrochemical/UHV techniques, Hubbard *et al.* [17-19] have characterized the adsorption of numerous aromatic molecules onto Pt(111) surfaces. In addition, it has been shown that some of these organic adsorbates may hinder, and in some cases inhibit, the deposition of copper and silver onto platinum substrates [20,21].

In contrast to the deposition of silver onto single crystal surfaces, quantitative voltammetric studies of silver electrodeposition onto polycrystalline platinum electrodes are complicated by the redox processes associated with oxide formation and reduction. The initial state of the platinum substrate can have a direct effect on the deposition and stripping behaviors. The present paper describes the differences

in voltammetric behavior on polycrystalline platinum electrodes for silver deposition and stripping resultant from the presence of co-adsorbed species as well as oxide coverage on the platinum electrode. The adsorbates studied were: pyrazine, pyridine, 4,4'-bipyridyl, 2,2'-bipyridyl, 4-phenylpyridine, 2-mercaptopyridine, and 4-mercaptopyridine. These were chosen as a group that incorporates N and S heteroatoms, as well as a systematic variation on electronic effects and structure. The results are compared to those from similar studies on Pt(111) electrodes.

Experimental

Working electrodes were Pt disks of approximately 0.010 cm^2 sealed in soft glass and polished with $1\text{ }\mu\text{m}$ diamond paste prior to use. The electrodes were rinsed with water and electrochemically cleaned in $0.10\text{M H}_2\text{SO}_4$ by continuous cycling between $+1.23\text{V}$ and -0.23V until the voltammetry indicative of a clean polycrystalline Pt surface was obtained. For experiments utilizing a bare, oxide-free Pt surface, this cycle was arrested at $+0.25\text{V}$ on the anodic sweep, in the so called 'double -layer' region prior to the formation of a platinum oxide layer. Conversely, the sweep was stopped at $+0.95\text{V}$ on the cathodic scan prior to oxide reduction for those studies involving an oxidized surface.

Evaluation of the electrochemical area was done through the integration of the voltammetric peaks for hydrogen adsorption. The charge corresponding to a hydrogen adatom monolayer was assumed to be $210\text{ }\mu\text{C}/\text{cm}^2$.

After electrochemical cleaning, the electrode was exposed, at open circuit, for three minutes to a solution of the adsorbate in either purified water or $0.10\text{M H}_2\text{SO}_4$. All solutions were 1.0 mM in the adsorbate of interest. This concentration has been determined to be at the limiting plateau from adsorption isotherms derived for each molecule [17-19]. The electrode was rinsed three times with a 0.10M sulfuric acid solution and then placed in a 1.0 mM silver solution in $0.10\text{M H}_2\text{SO}_4$.

The potential was then scanned at 10 mV/s in the negative direction starting at +0.85V.

All solutions were prepared using water purified by a Millipore Milli-Q system. Aqueous 0.10M sulfuric acid (Ultrex, J.T. Baker) was used as the supporting electrolyte. 0.5 mM Ag_2SO_4 solutions were prepared by dissolution of silver sulfate (Aldrich, 99.999%) in the base electrolyte. Pyrazine(99+%), 2,2'-bipyridyl (99+%), 4,4'-bipyridyl (98%), 4-phenylpyridine (99%), and 2-mercaptopyridine (99%) were used as received from Aldrich Chemical Co. 4-mercaptopyridine (tech, Aldrich) was recrystallized twice from absolute ethanol. Pyridine was distilled from CaH_2 prior to use.

Voltammograms were obtained using a BAS CV-27 potentiostat and data were recorded with a Soltec X-Y recorder. All potentials are referenced to a Ag/AgCl (sat'd NaCl) electrode without regard to the liquid junction potential. The uncertainty is approximately ± 5 mV. A large area coiled platinum wire was used as the counter electrode. A three-compartment electrochemical cell with provisions for degassing and solution exchange was used. Prior to use, all solutions were degassed with nitrogen which had been purified by passing through hydrocarbon and oxygen traps (MG Industries).

Results and discussion:

As a reference point for the following studies, the voltammetry for the underpotential deposition of silver from a 0.5 mM Ag_2SO_4 solution onto a polycrystalline platinum substrate is shown in Figure 1. This figure represents the voltammetric response for two consecutive scans over the UPD region beginning with a bare polycrystalline Pt electrode (i.e. nonoxidized, vide supra). It is clear that there are significant differences between the two voltammetric scans. When no oxide layer is initially present on the Pt surface (i.e. on the first scan, solid line), the

peak corresponding to the underpotential deposition of silver occurs at a potential of +0.630V while that attributed to bulk silver deposition occurs at a potential of +0.345V. The removal of the deposited silver also occurs over two regions during the subsequent anodic scan. A sharp stripping peak at a potential of +0.450V corresponds to the removal of bulk silver while the stripping of UPD silver occurs concurrent with the onset of oxide formation on the electrode surface in a broad, flat peak at +0.850V.

Upon formation of an oxide layer on the Pt surface, as seen in the subsequent cathodic scan (Figure 1: dashed line), the underpotential deposition of silver occurs at the more negative potential of +0.530V, corresponding to a 100 mV cathodic shift. It is believed that the presence of the oxide layer inhibits the deposition of silver thus leading to the observed potential shift. In such a case, the underpotential deposition of silver is precluded until reduction of the oxide layer begins, yielding bare Pt surface sites on which silver deposition may occur. Evidence for this is seen in Figure 1 through comparison of the second scan for silver deposition to a blank Pt voltammogram (Figure 1: dotted line). This clearly demonstrates that silver deposition is significantly hindered on the surface until the onset of oxide reduction at +0.750V. The charge of the resulting voltammetric peak attributed to the underpotential deposition of silver is much greater than that observed on a bare Pt surface due to the concurrent oxide reduction contribution. In addition to the negative shift in potential observed in the silver deposition peaks between the first and second sweeps, the silver stripping peaks are affected as well. In this case, the bulk stripping is split into two peaks occurring at potentials of +0.44V and +0.46V while the monolayer stripping is shifted to more positive potentials by 50 mV. These results are consistent with those reported by Arvía [6-8] and Szabo [2,3] in similar investigations of silver deposition on polycrystalline platinum substrates.

Arvíá has concluded that the peak at +0.44V corresponds to anodic stripping of the bulk silver phase whereas the peak at +0.46V corresponds to the anodic stripping of a second silver monolayer deposited just before the onset of bulk deposition [6]. Evidence for the formation of a second silver monolayer prior to bulk deposition has been reported in studies on Pt(111) by several authors [20,22-24]. In contrast, Szabo has attributed the doublet to the stripping of bulk silver from two structurally and energetically distinct surface sites [2,3]. The different sites are the result of different rates of oxide reduction from Pt(111) and Pt(100) sites present on the polycrystalline surface. After reduction of the first oxide, silver begins to deposit on these available surface sites and later the second reduction provides a new, distinct surface for the silver deposition process [2]. The structurally different deposits will then be stripped at two different potentials as observed.

It is expected that experiments involving silver deposition onto Pt electrodes pretreated with organic adsorbates will exhibit differences in the voltammetry discussed above. The voltammetric response resulting from deposition onto an adsorbate covered Pt surface will be compared with the corresponding peaks from the case where no adsorbate is present. Peak potentials associated with silver deposition and stripping are summarized in Table I for adsorption from purified water and Table II for adsorption from 0.10M H₂SO₄. The specific systems are discussed below.

1. *Pyrazine*

The voltammetry for silver deposition onto a bare Pt electrode pretreated with a 1.0 mM solution of pyrazine in water is shown in Figure 2A. The peak attributed to the underpotential deposition of silver is shifted by 30 mV in the negative direction to a potential of +0.600V. With pyrazine molecules blocking the platinum surface, deposition of silver should proceed at a slower rate. This effect is

evidenced by a broadened UPD peak with a significantly diminished charge. The observation of silver UPD indicates that the Ag/Pt interaction is stronger than the pyrazine/Pt interaction. The driving force needed to remove or displace the pyrazine layer is reflected in the shift to more negative potentials.

The onset of bulk deposition is shifted negatively by 35 mV in the presence of adsorbed pyrazine, but once begun, the deposition process peaks at nearly the same potential as in the adsorbate-free case. The voltammetric response is therefore much steeper in this region, indicating a kinetic control over the initiation of bulk deposition. The proposed kinetic control may be a direct consequence of adsorption of pyrazine to the silver monolayer. In addition to an overpotential necessary to initiate nucleation, an overpotential may also be required to drive the electron transfer across an adlayer of pyrazine. A combination of these effects leads to the initiation of bulk deposition at more negative values.

Stripping of bulk silver occurs at the same potential as in the adsorbate-free case. However, the pyrazine causes the removal of the UPD silver overlayer to be shifted to more positive potentials by 30 mV, as shown in Table I. This shift suggests that the pyrazine molecules return to the interface as bulk silver is removed and stabilize the remaining silver monolayer. This potential region in the anodic sweep also represents the onset of PtO formation. Figure 2B is the voltammetry obtained for silver deposition onto a PtO surface which has been exposed to a 1.0 mM solution of pyrazine in water. The voltammetric response is virtually identical to the dashed line shown in Figure 1. It appears that once the oxide film forms, pyrazine molecules are unable to bind to the electrode. This suggests that the oxygen-platinum interaction is significantly stronger than the nitrogen-platinum interaction binding pyrazine to the Pt substrate.

The voltammetric response for silver deposition on an electrode pretreated with a 1.0 mM pyrazine solution in 0.10M H₂SO₄ is nearly identical to that described

above. Since pyrazine has a pK_a of +0.68 it remains largely unprotonated in a 0.10M H_2SO_4 solution. There are no appreciable differences in the UPD nor bulk deposition regions of the voltammetry from that described above.

2. Pyridine

Successive voltammetric scans for silver deposition onto an initially oxide-free, bare Pt surface pretreated with 1.0 mM pyridine in water are shown in Figure 3A. Here it is seen that on the initial scan the UPD peak is shifted negatively by 40 mV to a potential of +0.590V. The onset of bulk deposition is suppressed by 50 mV, but as in the previous case, peaks at the same potential as for the adsorbate-free Pt substrate. Again, kinetic control of the nucleation and charge transfer likely accounts for this effect.

The bulk silver stripping peak occurs at +0.450V, consistent with the results for a clean Pt surface. However, the monolayer stripping peak is shifted to more positive potentials by 25 mV in the presence of the pyridine adsorbate. This region also represents the onset of oxide formation, and the observed shift may be due to a displacement of the PtO contribution to more positive potentials as a result of Pt/Ag/adsorbate interactions.

When compared to the effects on silver deposition produced by the adsorption of pyrazine, pyridine appears to be more effective at hindering the deposition. Studies by Wieckowski *et al.* have demonstrated that pyridine will interact with polycrystalline platinum via the nitrogen lone pair and adopt a vertical adsorption geometry [25]. Studies of pyrazine adsorption onto a Pt(111) surface by Hubbard *et al.* have shown that this heterocycle binds to the surface through one of the nitrogen atoms as well, at a near vertical angle of 79° [17]. The molecular footprints for pyridine and pyrazine will be nearly identical; however, the Pt/adsorbate interaction strengths might be anticipated to be different as a result of

the second nitrogen atom present on the pyrazine ring but absent on pyridine. Since nitrogen is more electronegative than carbon, there should be less charge transfer and a weaker bond between Pt and pyrazine when compared with the interaction between Pt and pyridine. Inspection of the voltammetries reveals that for the case of pyridine, the UPD peak is broader, flatter, and consisting of less charge than for the pyrazine case. We conclude that because of the proposed weaker interaction with Pt, pyrazine is displaced by UPD silver at more positive potentials and at a faster rate than pyridine. In other words, pyridine exhibits a stronger inhibiting effect.

In contrast, when the electrode is pretreated with a solution of pyridine in 0.10M H_2SO_4 (Figure 3B), the voltammetry is essentially identical to that for deposition onto a clean, bare polycrystalline platinum substrate. Since pyridine has a pK_a value of 5.25, it would be expected that in a 0.10M H_2SO_4 solution the ring nitrogen would be protonated, thus precluding adsorption of the molecule onto the platinum surface through the nitrogen site. There was, however, one significant effect arising from the pretreatment of the electrode with the protonated pyridine molecules. The bulk deposition peak is again shifted to more negative potentials and in addition it is much steeper, indicating a hindrance to the charge transfer necessary for bulk deposition. The pyridine molecules may have adsorbed weakly onto the platinum electrode surface through the π system of the aromatic ring, accounting for this effect without there being a strong enough interaction to hinder silver UPD. Previous studies by Wieckowski *et al.* have shown that pyridine molecules can adsorb in this manner at low concentrations [25].

3. 2,2'-bipyridyl

The voltammetry for silver deposition onto a polycrystalline platinum electrode pretreated with a 1.0 mM solution of 2,2'-bipyridyl in purified water is shown in Figure 4A. The first scan shows deposition onto an oxide-free platinum

substrate, and it is evident that the deposition process has been altered from that for the adsorbate-free case shown in Figure 1. The UPD peak occurs at +0.595V, representing a shift to more negative potentials by 35mV. Additionally, the peak has broadened, and consists of less charge than the corresponding deposition peak in Figure 1. The bulk deposition is shifted negatively by 80 mV and also exhibits the characteristic wave indicating kinetic control.

The ring nitrogens of 2,2'-bipyridyl are situated such that their simultaneous access to the substrate is hindered by H atoms at the 3 and 3' positions on the rings. The possible adsorption conformations are a horizontal orientation with coplanar rings or a twisted conformation with one ring perpendicular and the other ring parallel to the metal surface. Studies by Hubbard *et al.* have shown 2,2'-bipyridyl to adsorb onto Pt(111) surfaces in the twisted manner, interacting through one nitrogen site and the π system of the adjoining ring [17]. The resulting large molecular footprint of this conformation may account for the shifts to more negative potentials and changes in the peak shapes evidenced in both the UPD and bulk deposition regions.

The second scan in Figure 4A (dashed line) shows the voltammetric response after an oxide layer has formed over the platinum surface. The experiments done with adsorption of 2,2'-bipyridyl onto a Pt surface covered with an oxide film also support the assertion that nitrogen-bonding adsorbates may not displace the oxide film from the platinum electrode since this scan is identical to the adsorbate free scan in Figure 1.

When the electrode is pretreated with a solution of 2,2'-bipyridyl in 0.10M H₂SO₄ (Figure 4B), the voltammetric response approaches that of the adsorbate-free case. The UPD peak is shifted by only 15 mV to +0.615V and the onset of bulk deposition is only shifted by 20 mV; both to more cathodic potentials. Since the first pK_a value for 2,2'-bipyridyl is 4.44, it would be expected that in 0.10M H₂SO₄

solution at least one of the ring nitrogens would be protonated. Studies on Pt(111) have shown that the voltammetry for underpotential deposition of silver is completely unaffected by pretreatment of the electrode with a 1.0 mM solution of 2,2'-bipyridyl in 0.10M H₂SO₄ [20]. However, contrary to the single crystal case, the voltammetry on a polycrystalline platinum electrode is altered considerably. Since protonated molecules are less likely to adsorb to platinum, the stepped sites, kinks, and other types of surface defects existing on the polycrystalline platinum surface (and much less prevalent on Pt(111)) must be energetically favorable for deprotonation and result in the adsorption of the molecule. The interaction of the adsorbate with the platinum substrate may hinder both the UPD and bulk deposition processes by blocking the disordered sites favorable for deprotonation and adsorption. Adsorption in a "face on" geometry through the π system (as suggested with protonated pyridine) would not be expected to affect the UPD process since the adsorption bond is much weaker than a Pt-N interaction.

4. 4,4' bipyridyl

When a polycrystalline platinum electrode is pretreated with a 1.0 mM solution of 4,4'-bipyridyl in water, the voltammetric behavior for the deposition of silver is as shown in Figure 5A. Silver UPD onto an oxide-free platinum substrate (first scan in Figure 5A) takes place in a broad peak centered at +0.575V. The onset of bulk deposition is inhibited by 70 mV before proceeding, very rapidly, to a sharp deposition peak at +0.340V. The shifts in silver UPD (55mV) and in the onset of bulk silver deposition are larger than those seen in the cases of pyridine, pyrazine, and 2,2'-bipyridyl. A qualitative comparison of the voltammetric scans also reveals that for the case of 4,4' bipyridyl the UPD peak is broadest and has the smallest charge. This would indicate that 4,4'-bipyridyl has a stronger interaction with the platinum electrode surface than any of the previously considered adsorbates.

Measurements of the molecular packing density of 4,4'-bipyridyl adsorbed onto platinum from a 1.0 mM solution indicate that the molecule is bound in a nearly vertical conformation [15]. EELS studies have also confirmed the existence of out-of-plane C-H bending modes, suggesting that one pyridine ring is not interacting with the substrate [18]. This evidence indicates that the second nitrogen site is completely free of the platinum surface and may interact with the silver ions in solution. Although 2,2'-bipyridyl also contains two nitrogen atoms, the second pyridine ring of 2,2'-bipyridyl is twisted down toward the platinum substrate, effectively blocking the nitrogen site. Furthermore, pyrazine, pyridine, and 2,2'-bipyridyl all adsorb in a manner that yields an adsorbate layer one ring thick. 4,4'-bipyridyl adsorbs vertically, resulting in an adsorbate layer that is approximately twice as thick. It is conceivable that the approach of the silver ions in solution to the electrode surface is hindered by an inability to diffuse through the thicker adsorbate layer. In addition, there could be inhibitive effects due to coordination by the free pyridine nitrogen on 4,4'-bipyridyl with silver ions in solution. The large degree of rotational freedom of a second pyridine ring is expected to make silver coordination with 4,4'-bipyridyl nitrogens more significant than the analogous coordination with pyrazine nitrogens.

The second scan in Figure 5A demonstrates the voltammetric response after the onset of platinum oxide formation. In complete consistency with all three preceding adsorbates studied, the voltammetry does not display any differences from the adsorbate-free case shown in Figure 1.

The deposition of silver onto an electrode pretreated with a solution of 4,4'-bipyridyl in 0.10M H₂SO₄ is shown in Figure 5B. In this case, the UPD peak is shifted negatively by only 20 mV to +0.610V. Bulk deposition now begins at +0.420V on the cathodic scan; a shift of only 30 mV. The bipyridyl ring nitrogens are expected to be protonated in a 0.10M H₂SO₄ solution since the first pK_a value for this molecule is

4.87. However, studies on the adsorption of this molecule from acid solution onto Pt(111) reveal that the second nitrogen site can be easily deprotonated due to electron density withdrawing effects transferred through the molecule [20]. The result is one protonated nitrogen site with a net positive charge, and one nitrogen site available for chemisorption to the platinum substrate. The repulsive effects arising from interactions between the positive charges may cause the adsorbate layer to be less densely packed, thus the deposition of silver is less hindered than when adsorption occurs from water.

5. *4-phenylpyridine*

The voltammetry for the deposition of silver onto a polycrystalline platinum electrode pretreated with a 1.0 mM solution of 4-phenylpyridine in water is shown in Figure 6A. Underpotential deposition is almost completely inhibited, as evidenced by the broad, flat peak centered between +0.530V and +0.560V. The shift in this peak as a result of the 4-phenylpyridine overlayer is of the order of 85 mV. The bulk deposition displays the same kinetic limitations observed with the previous adsorbates. Bonding to the Pt electrode through the lone nitrogen site, adsorption of 4-phenylpyridine will yield an adsorbate layer two rings thick and structurally similar to the previously discussed 4,4' bipyridyl. However, comparison of the resultant voltammetries during deposition of silver shows that 4-phenylpyridine is significantly more effective at hindering deposition. The UPD peak in the 4-phenylpyridine case is much flatter and consists of much less charge. The comparison between 4-phenylpyridine and 4,4' bipyridyl is analogous to the comparison between pyridine and pyrazine. Again, the electron withdrawing effects of a second nitrogen atom decrease the charge transfer between Pt and the first nitrogen atom, leading to a weaker interaction. Although the two molecules have comparable packing densities and molecular footprints, the strength of the

Pt/adsorbate interaction may be much greater in the 4-phenylpyridine case. The combination of interaction strength and adsorbate layer thickness results in making 4-phenylpyridine the most effective of all five nitrogen-bonding adsorbates at hindering the silver deposition process. However, further experiments have shown that oxide formation precludes chemisorption of the 4-phenylpyridine to the platinum surface. This result is consistent with the previous results from adsorbates bonding to the platinum through a nitrogen atom.

The voltammetry of silver deposition onto an electrode pretreated with 4-phenylpyridine in 0.10M H_2SO_4 , shown in Figure 6B, indicates that some adsorption of the molecule takes place due to the shifts in UPD and bulk deposition peaks. Studies on Pt(111) have shown the nitrogen site to be protonated and the molecule completely unable to adsorb to the single crystal surface at this pH [20]. The adsorption of ostensibly protonated 4-phenylpyridine onto a polycrystalline platinum electrode is most likely due to the presence of highly energetic surface sites which do not exist on single crystal faces. Adsorption of 4-phenylpyridine at low pH does not effect as much hindrance as is observed from adsorption at higher pH. The UPD peak now occurs at +0.600V, a shift of only 30 mV from the adsorbate-free case. There is also a shift of only 25 mV in the onset of bulk deposition. These results are consistent with results found from the previously discussed case of 2,2'-bipyridyl in 0.10M H_2SO_4 .

6. 4-mercaptopyridine

Figure 7A presents the voltammetric response for silver deposition onto a platinum electrode pretreated with a 1.0 mM solution of 4-mercaptopyridine in water. The voltammetry indicates that a very strong interaction exists between this adsorbate and the polycrystalline platinum surface. The UPD of silver is completely inhibited, and the onset of bulk deposition is inhibited by 130 mV. The bulk

deposition peak occurs at +0.290V, and bulk silver stripping is the only observable process occurring during the anodic scan. A single, sharp peak exists at +0.490V, indicating a shift of 25 mV to more positive potentials for the oxidative process. There is no evidence of UPD silver stripping, indicating that 4-mercaptopyridine molecules immediately displace the silver monolayer following bulk stripping. Furthermore, the formation of platinum oxide does not occur in the presence of adsorbed 4-mercaptopyridine, and thus subsequent scans are nearly identical to the initial scan. There is also a prominent hysteresis loop as a result of the significant overpotential necessary to initiate bulk deposition. Similar voltammetry for silver deposition has been found on Pt(111) surfaces [20].

The voltammetric evidence suggests that 4-mercaptopyridine forms an adsorbate bond of significantly higher strength than any of the other adsorbates previously considered. This adsorbate has been shown to chemisorb to a silver surface through the sulfur atom rather than the nitrogen site as would be anticipated [19]. The inhibitive effects evidenced in the voltammetry discussed above as well as voltammetric results from experiments where pretreatment of the electrode was effected with a solution of 4-mercaptopyridine in 0.10M H₂SO₄ (Figure 7B) suggest that adsorption is through the sulfur site on polycrystalline platinum surfaces as well. At a pH of 1.0 or less, the 4-mercaptopyridine nitrogen sites will be protonated, yet the voltammetry is not significantly affected. Since the nitrogen site is located *para* to the sulfur, a sulfur-platinum bond would cause the nitrogen to be directed away from the surface.

The voltammetric response is the same as that described above when an oxide covered polycrystalline platinum surface is exposed to a 1.0 mM solution of 4-mercaptopyridine in water. The sulfur-platinum bond appears to be stronger than the PtO bond and is, therefore, the strongest of the three interactions studied.

7. 2-mercaptopyridine

The voltammetric scan for the deposition of silver onto a polycrystalline platinum electrode pretreated with 2-mercaptopyridine in water is shown in Figure 8A. Again, the only process seen to occur is the deposition and stripping of bulk silver. Underpotential deposition and oxide formation are completely inhibited by the presence of 2-mercaptopyridine. The bulk deposition peak occurs at +0.270V, a shift to negative potentials of 20 mV more than seen with 4-mercaptopyridine. The bulk stripping process results in a double peak at +0.465V and +0.505V not seen with 4-mercaptopyridine as the co-adsorbate. These two peaks could ostensibly be due to the bridging ability of 2-mercaptopyridine. If the molecule binds primarily through the sulfur atom [19], the nitrogen site will be rigidly positioned in close proximity to the platinum surface. This may result in a second adsorbate-platinum interaction and give rise to the observed double peak.

The double peak may also result from energetically distinct sites on the polycrystalline platinum surface. Studies of silver deposition onto Pt(111) in the presence of a 2-mercaptopyridine adlayer reveal further evidence for a chelate adsorption model, but have not shown any evidence of a double peak during the anodic scan [20]. Further experiments with polycrystalline platinum electrodes have shown that the relative peak heights associated with the stripping of bulk silver are affected by varying the oxide layer coverage prior to adsorption of the 2-mercaptopyridine and subsequent silver deposition. The potential at which the preparatory cyclic voltammogram is arrested will determine the extent of oxide coverage during adsorption of 2-mercaptopyridine. As the oxide coverage is increased, the double peak, representing the oxidation of bulk silver, shifts to more positive potentials, increasing the relative charge beneath the more positive peak. The comparison with studies on Pt(111), the above mentioned voltammetric evidence, and Szabo's conclusion that oxide formation occurs over two energetically

distinct sites [2,3] all suggest that the double peak observed during the removal of bulk silver from a polycrystalline platinum substrate with 2-mercaptopyridine as a co-adsorbate is the result of adsorbate bridging effects enhanced by the existence of distinct sites present on the polycrystalline surface.

The pKa of 2-mercaptopyridine is reported to be 1.07, which is similar to the pH of a 1.0 mM solution of 2-mercaptopyridine in 0.10M H₂SO₄. Figure 8B represents the deposition of silver onto a platinum electrode pretreated with 2-mercaptopyridine in a 0.10M H₂SO₄ solution. There are no significant variations in the voltammetric response.

Conclusions

In this study we have characterized the deposition of Ag onto polycrystalline platinum electrodes pretreated with various adsorbates. The presence of organic co-adsorbates has provided a great deal of insight into the electrodeposition mechanism. Our observations are consistent with a Pt/Ag/adsorbate structure. Bulk deposition was shown to be dominated by kinetic control of the charge transfer across the adsorbate layer. Each co-adsorbate was shown to inhibit the deposition processes to an extent determined by a combination of packing density, molecular footprint, adsorbate layer thickness, and adsorption strength. The deposition of silver onto a non-uniform polycrystalline platinum surface has been contrasted with deposition onto Pt(111). We believe that the polycrystalline surface provides highly energetic (kinks and steps) sites which are thermodynamically favorable for deprotonation and subsequent adsorption of heterocyclic organic molecules.

Future studies will focus on the deposition of silver onto polycrystalline platinum electrodes in the presence of oxygen containing adsorbates. The effects of disordered surface sites, pH, and adsorbate concentration will be studied and compared to these results and to previous studies on Pt(111) surfaces.

Acknowledgments

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Table I**Summary of Peak Positions for Nitrogen Bonding Adsorbates**Deposition/Stripping Potentials (V) of Ag⁺ onto a Pt Substrate vs. Ag/AgCl

Adsorbate	Solvent	UPD	UPD Stripping	Bulk	Bulk Strip
None	PDW	+0.630	+0.850	+0.345	+0.450
44BPY	PDW	+0.575	+0.900	+0.330	+0.445
22BPY	PDW	+0.595	+0.900	+0.340	+0.445
4PP	PDW	+0.560	+0.900	+0.335	+0.450
Pyrazine	PDW	+0.600	+0.880	+0.345	+0.450
Pyridine	PDW	+0.590	+0.875	+0.345	+0.450
44BPY	.10M H ⁺	+0.610	+0.900	+0.340	+0.450
22BPY	.10M H ⁺	+0.605	+0.875	+0.340	+0.450
4PP	.10M H ⁺	+0.600	+0.900	+0.340	+0.450
Pyrazine	.10M H ⁺	+0.610	+0.875	+0.345	+0.450
Pyridine	.10M H ⁺	+0.625	+0.850	+0.345	+0.450

Deposition/Stripping onto a PtO Surface

None	PDW	+0.530	+0.900	+0.330	+0.44, +0.46
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All five adsorbates are unable to adsorb onto a PtO surface and thus all voltammetry over PtO surfaces showed the same potentials as above. Furthermore, formation of PtO on a bare Pt surface previously exposed to any of the above adsorbates would result in the removal of the adsorbate layer.

PDW = Purified water

44BPY = 4,4' Bipyridyl

22BPY = 2,2' Bipyridyl

4PP = 4-Phenylpyridine

Table II**Summary of Peak Positions for Sulfur Bonding Adsorbates**Deposition/Stripping Potentials (V) of Ag⁺ onto a Pt Substrate vs. Ag/AgCl

Adsorbate	Solvent	UPD	UPD Stripping	Bulk	Bulk Strip
None	PDW	+0.630	+0.850	+0.345	+0.450
4MP	PDW	NA	NA	+0.290	+0.490
2MP	PDW	NA	NA	+0.280	+0.46, +0.50
4MP	.10M H ⁺	NA	NA	+0.290	+0.490
2MP	.10M H ⁺	NA	NA	+0.280	+0.46, +0.50

4MP = 4-mercaptopyridine

2MP = 2-mercaptopyridine

Figure Captions

Figure 1: Deposition of silver from a 1 mM silver solution in 0.10M H₂SO₄ onto a bare polycrystalline platinum electrode starting at +0.82 V. (—) Initial scan, no PtO present. (- - -) Second scan, after PtO formation. , (---) Blank Pt cyclic voltammogram in 0.10M H₂SO₄. Scan Rate = 10.0 mV/s. Electrode area = 0.010 cm².

Figure 2: Deposition of silver from a 1 mM silver solution in 0.10M H₂SO₄ onto a bare polycrystalline platinum electrode pretreated with 1mM pyrazine in water. (A) (---) Ag deposition onto a bare Pt surface. (B) (—) Ag deposition onto a PtO surface, (—) Ag deposition onto a PtO surface after exposure to a 1.0 mM solution of pyrazine in water. Experimental parameters are the same as in Figure 1.

Figure 3: Deposition of silver from a 1 mM silver solution in 0.10M H₂SO₄ onto a bare polycrystalline platinum electrode pretreated with 1mM pyridine in (A) water. (—) Initial scan, (---) second scan; and (B) 0.10M H₂SO₄. (---) Ag deposition onto a bare Pt surface. Experimental parameters are the same as in Figure 1.

Figure 4: Deposition of silver from a 1 mM silver solution in 0.10M H₂SO₄ onto a bare polycrystalline platinum electrode pretreated with 1mM 2,2'-bipyridyl in (A) water. (—) Initial scan, (---) second scan; and (B) 0.10M H₂SO₄. (---) Ag deposition onto a bare Pt surface. Experimental parameters are the same as in Figure 1.

Figure 5: Deposition of silver from a 1 mM silver solution in 0.10M H₂SO₄ onto a bare polycrystalline platinum electrode pretreated with 1mM 4,4'-bipyridyl in (A) water. (---) Initial scan, (—) second scan; and (B) 0.10M H₂SO₄. (---) Ag deposition onto a bare Pt surface. Experimental parameters are the same as in Figure 1.

Figure 6: Deposition of silver from a 1 mM silver solution in 0.10M H₂SO₄ onto a bare polycrystalline platinum electrode pretreated with 1mM 4-phenylpyridine in (A) water. (–) Initial scan, (---) Ag deposition onto a bare Pt surface; and (B) 0.10M H₂SO₄. (---) Ag deposition onto a bare Pt surface. Experimental parameters are the same as in Figure 1.

Figure 7: Deposition of silver from a 1 mM silver solution in 0.10M H₂SO₄ onto a bare polycrystalline platinum electrode pretreated with 1mM 4-mercaptopyridine in (A) water. (–) Initial scan, (---) Ag deposition onto a bare Pt surface; and (B) 0.10M H₂SO₄. Experimental parameters are the same as in Figure 1.

Figure 8: Deposition of silver from a 1 mM silver solution in 0.10M H₂SO₄ onto a bare polycrystalline platinum electrode pretreated with 1mM 2-mercaptopyridine in (A) water. (–) Initial scan, (---) Ag deposition onto a bare Pt surface; and (B) 0.10M H₂SO₄. Experimental parameters are the same as in Figure 1.

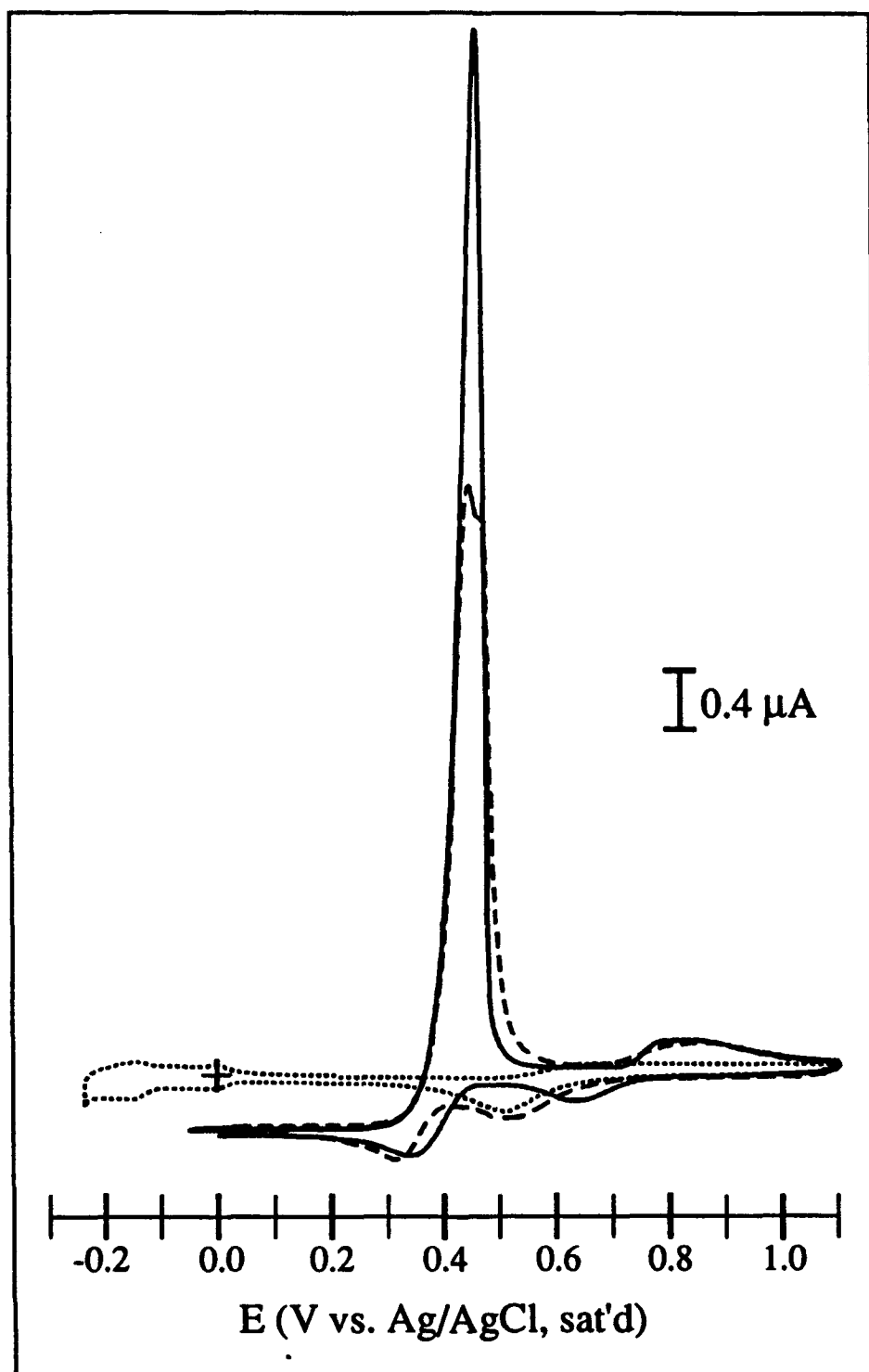


Figure 1

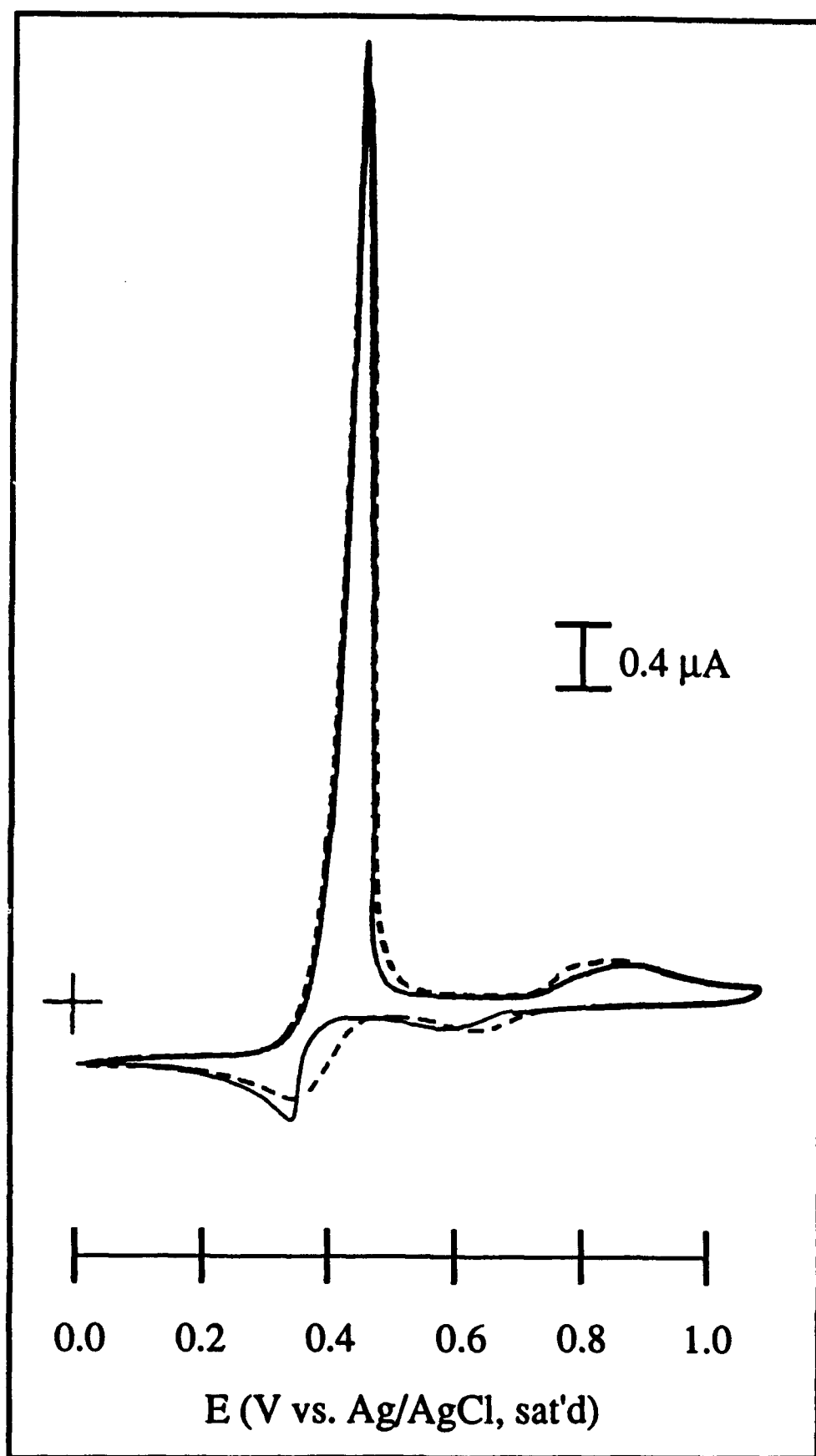


Figure 2A

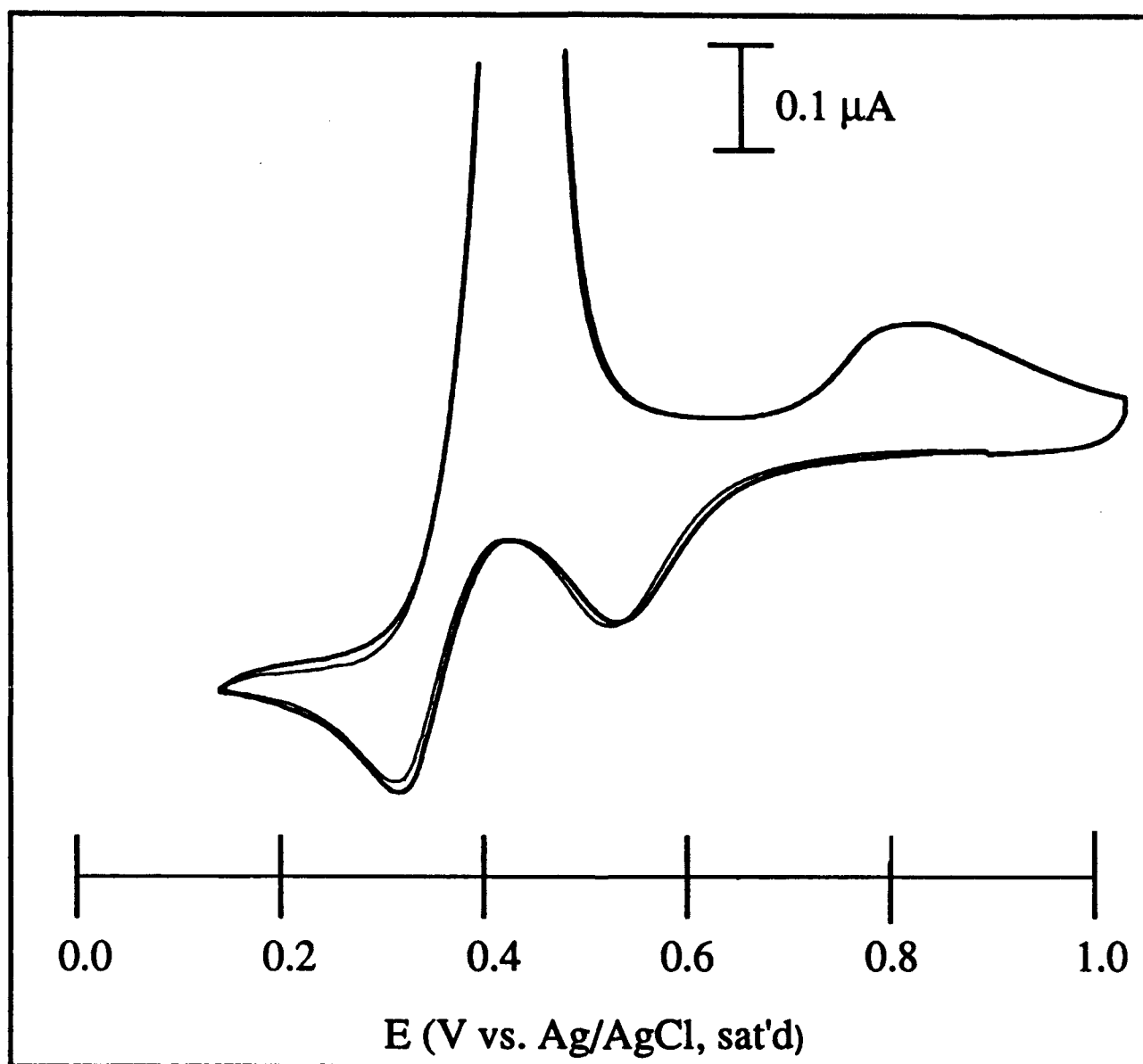


Figure 2B

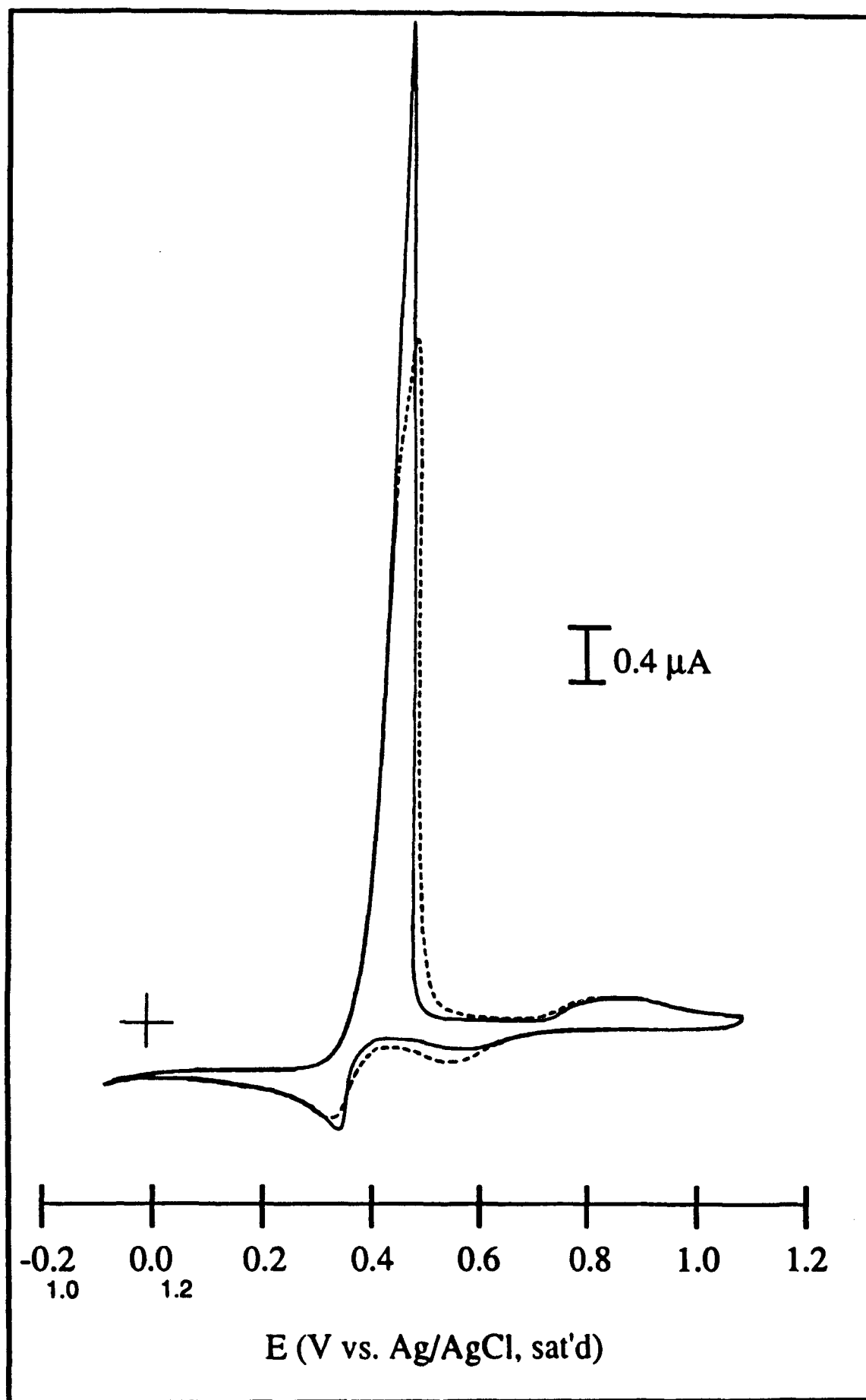


Figure 3A

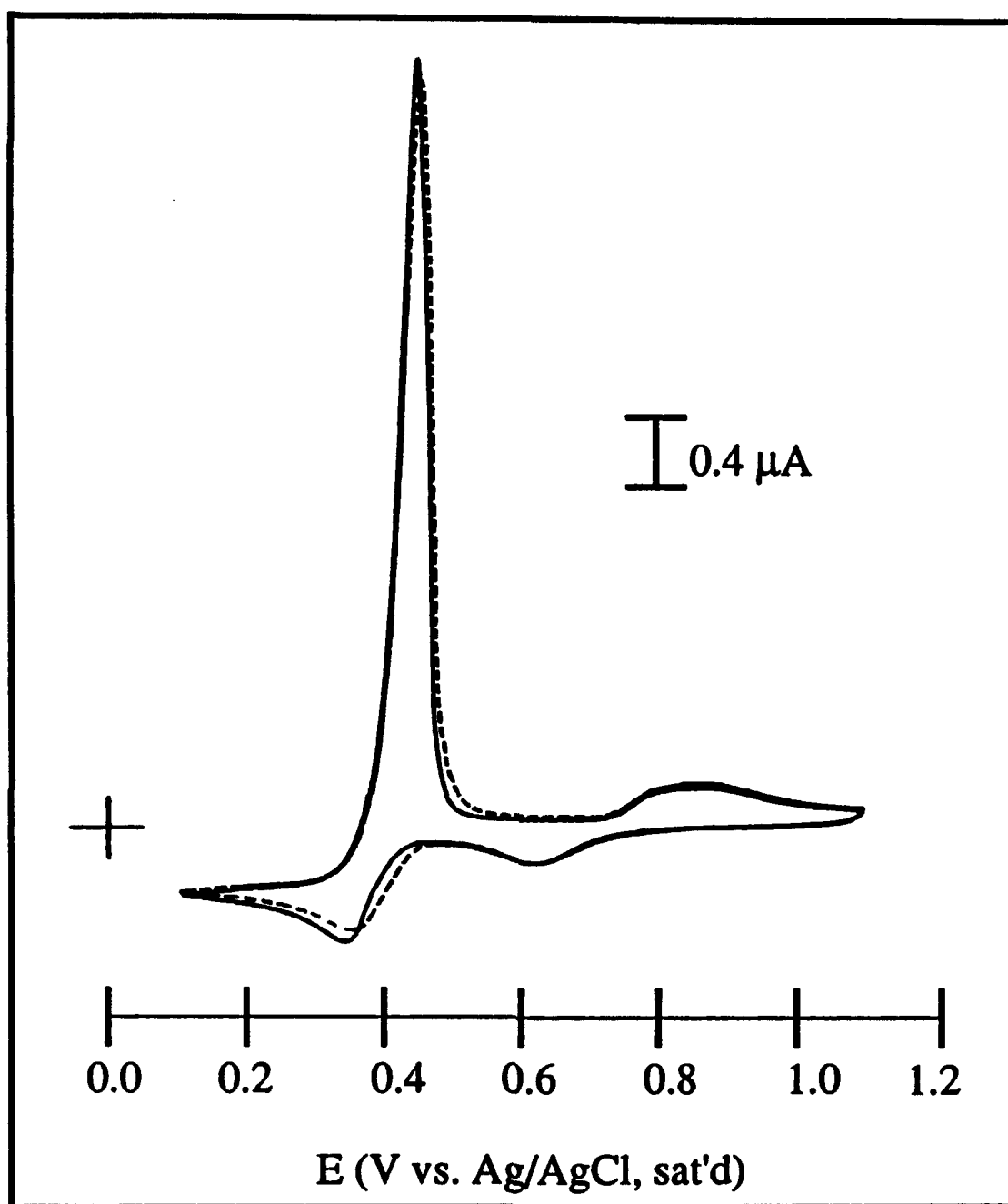


Figure 3B

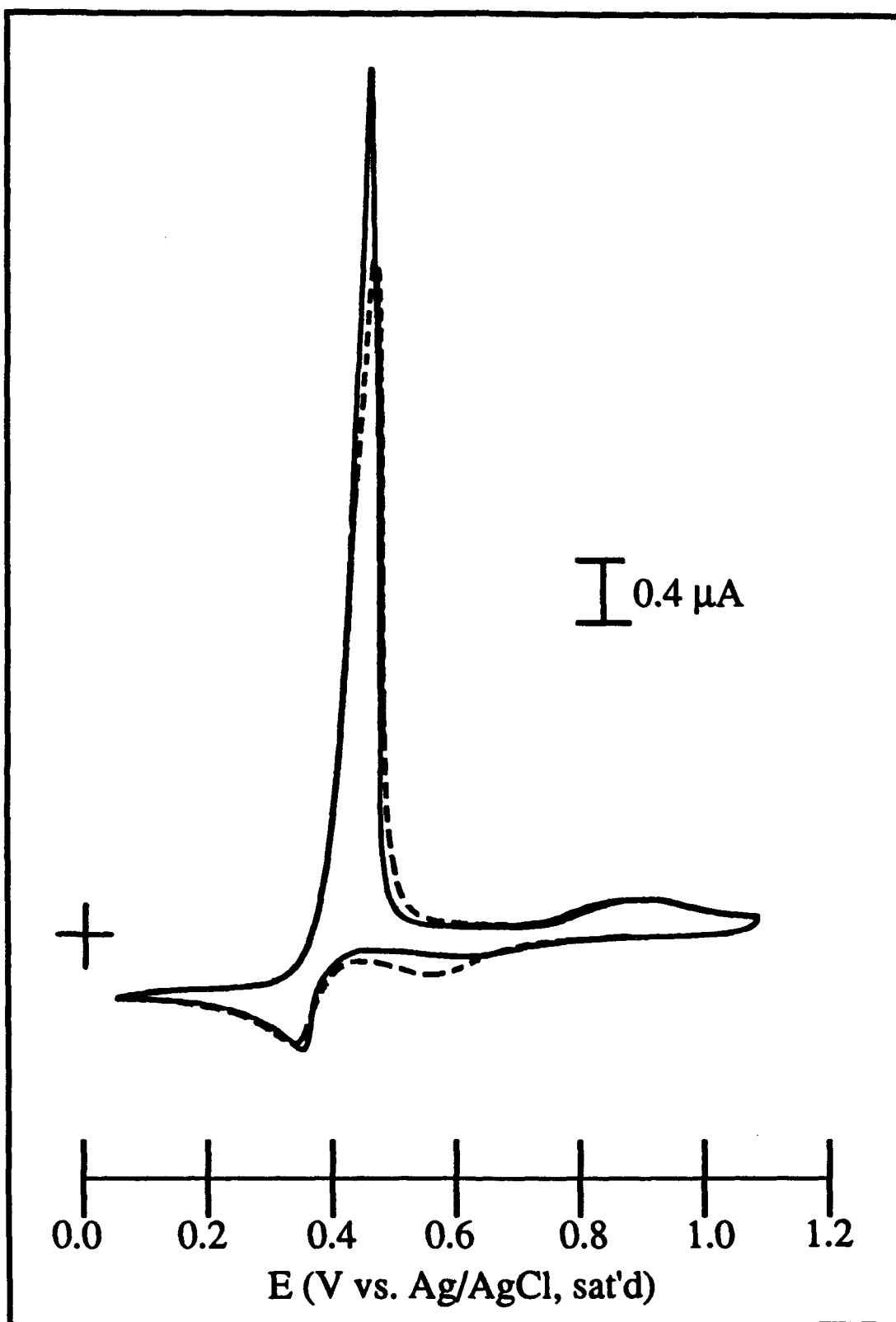


Figure 4A

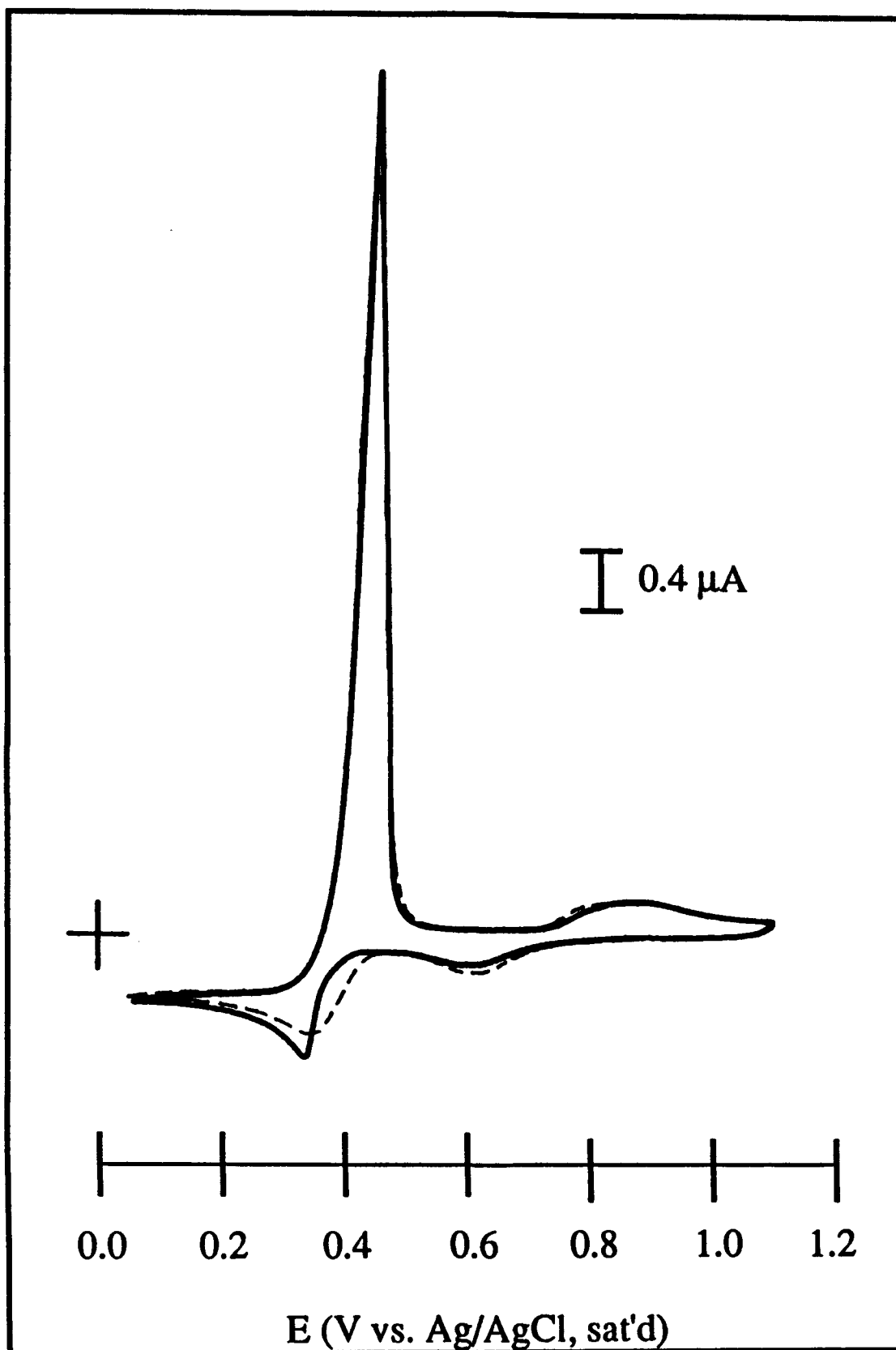


Figure 4B

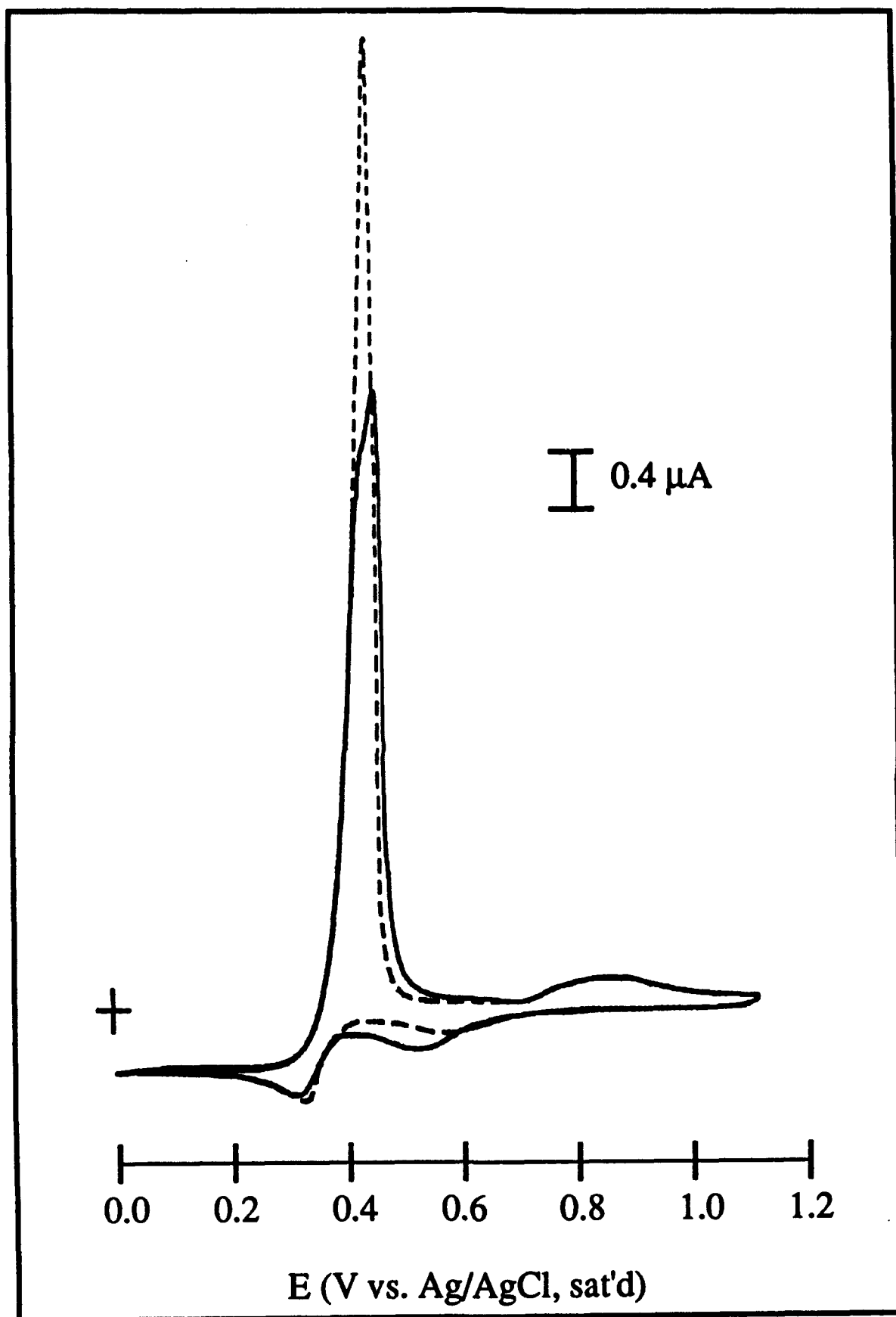


Figure 5A

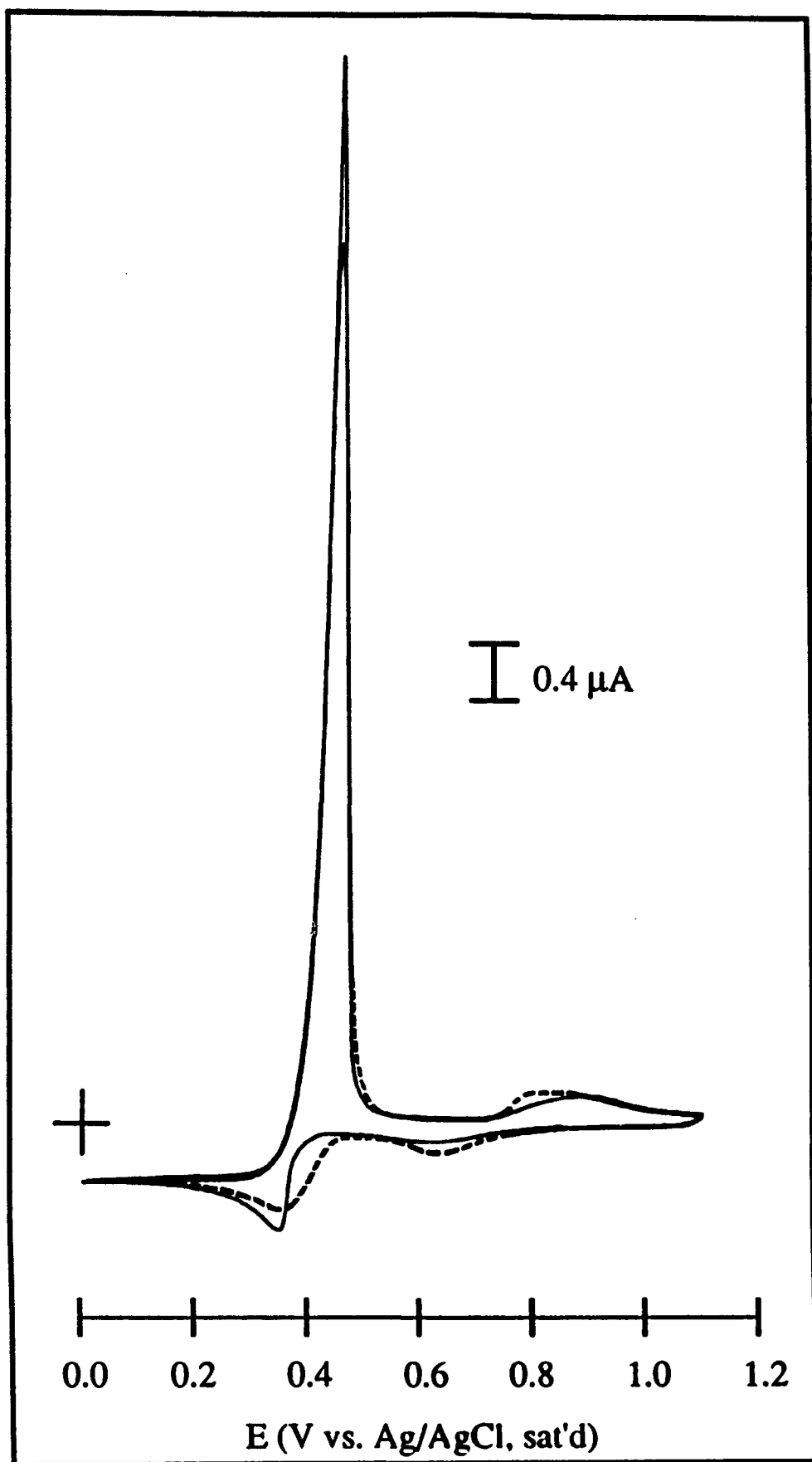


Figure 5B

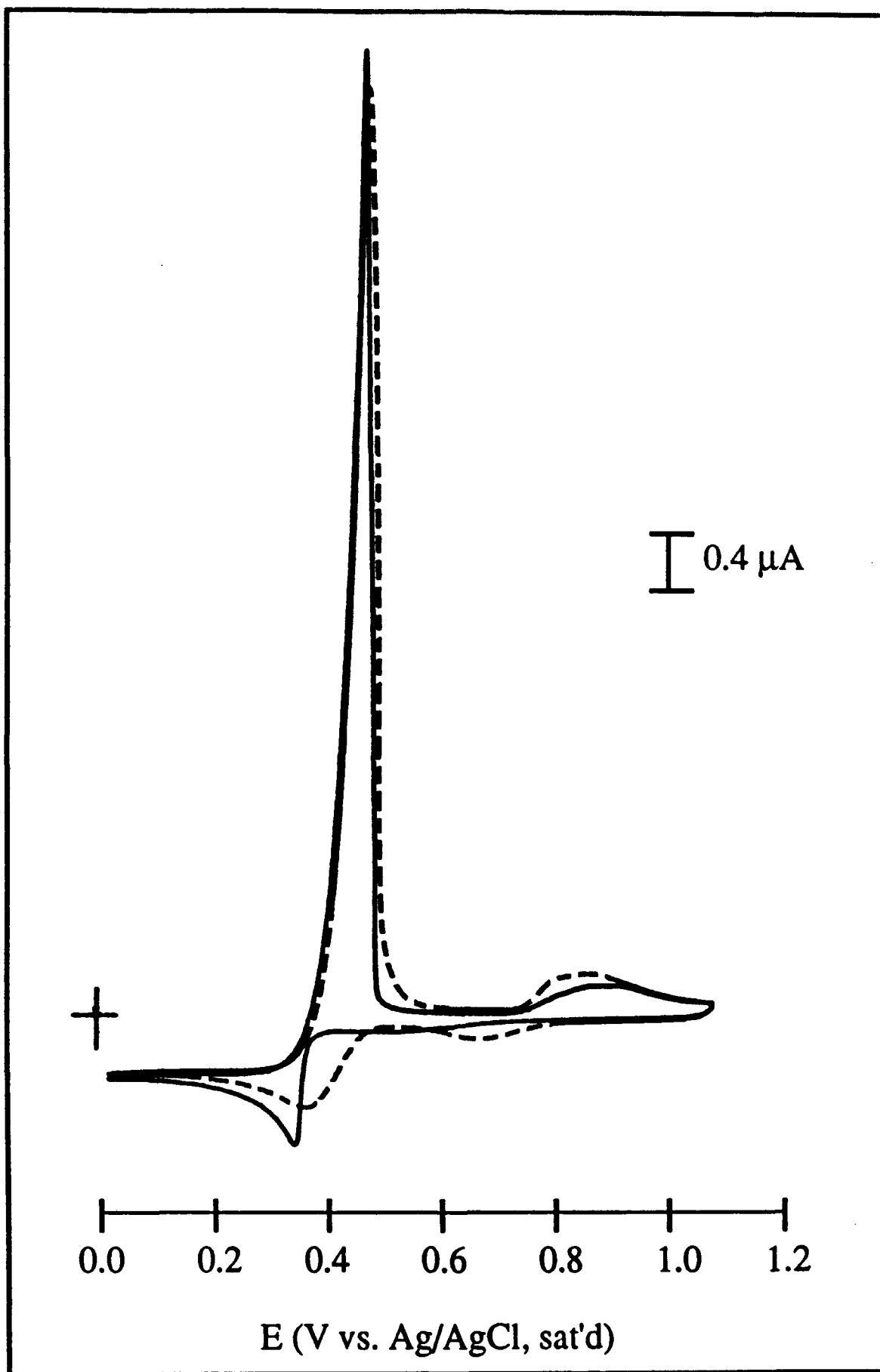


Figure 6A

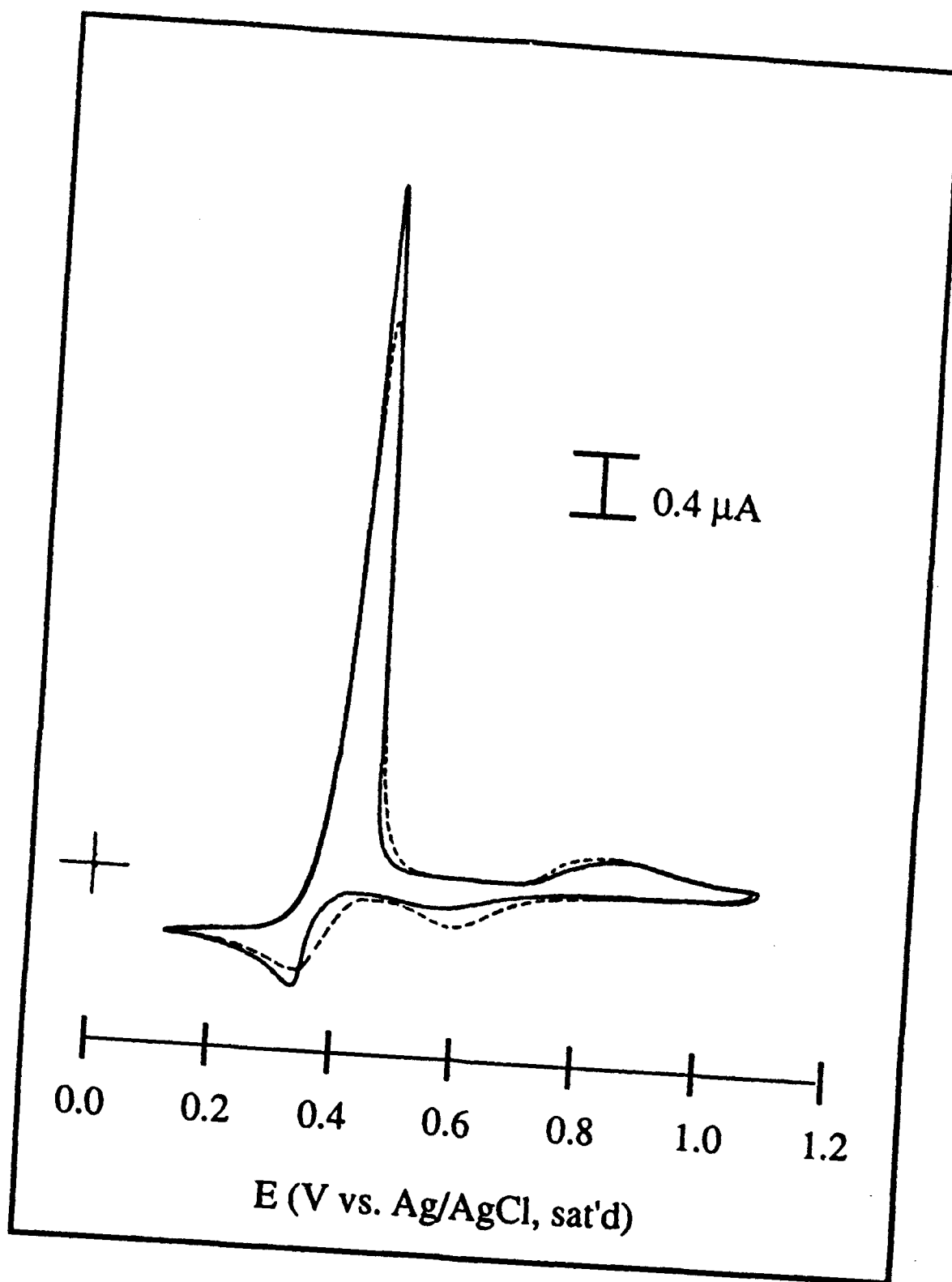


Figure 6B

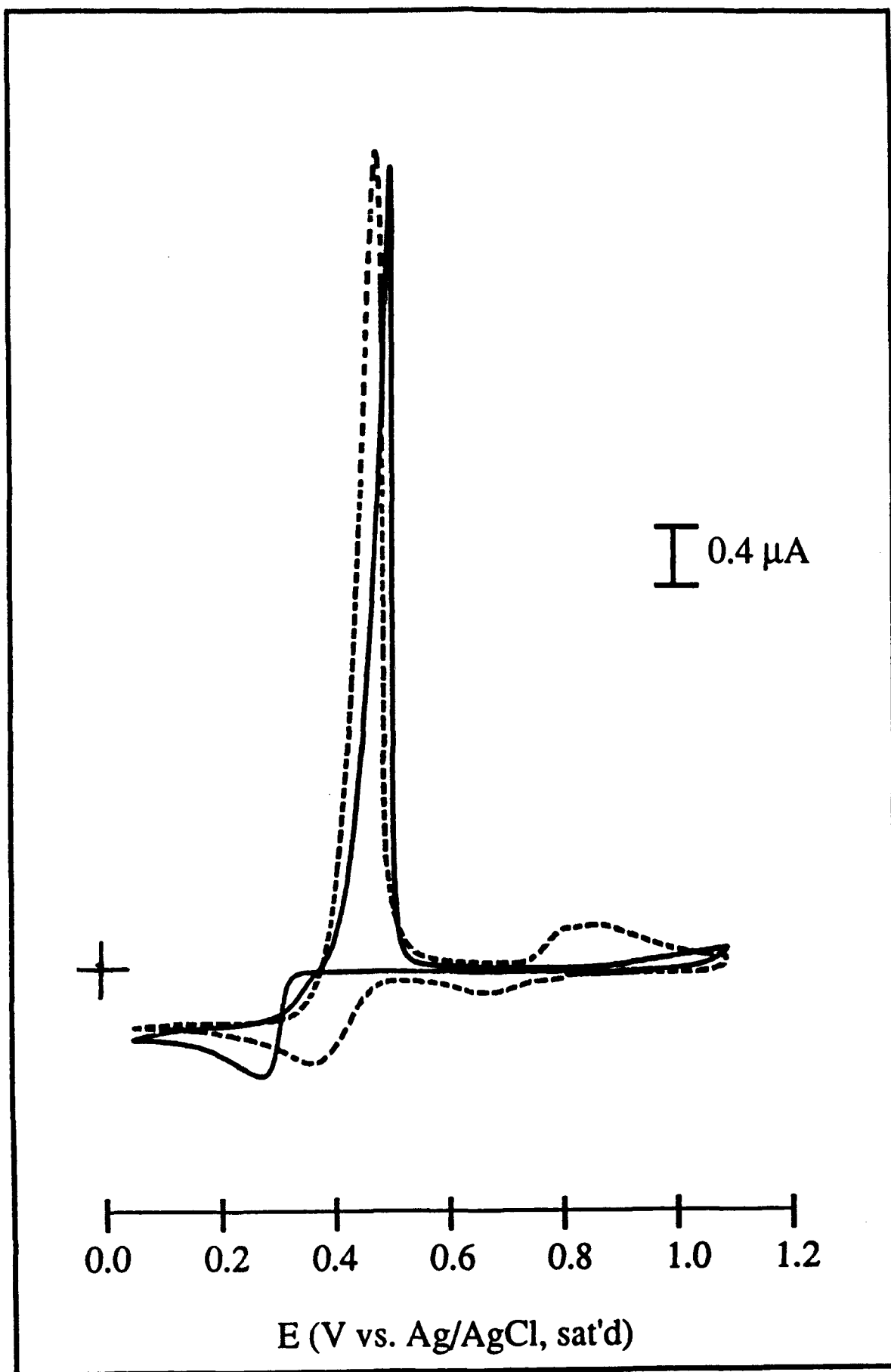


Figure 7A

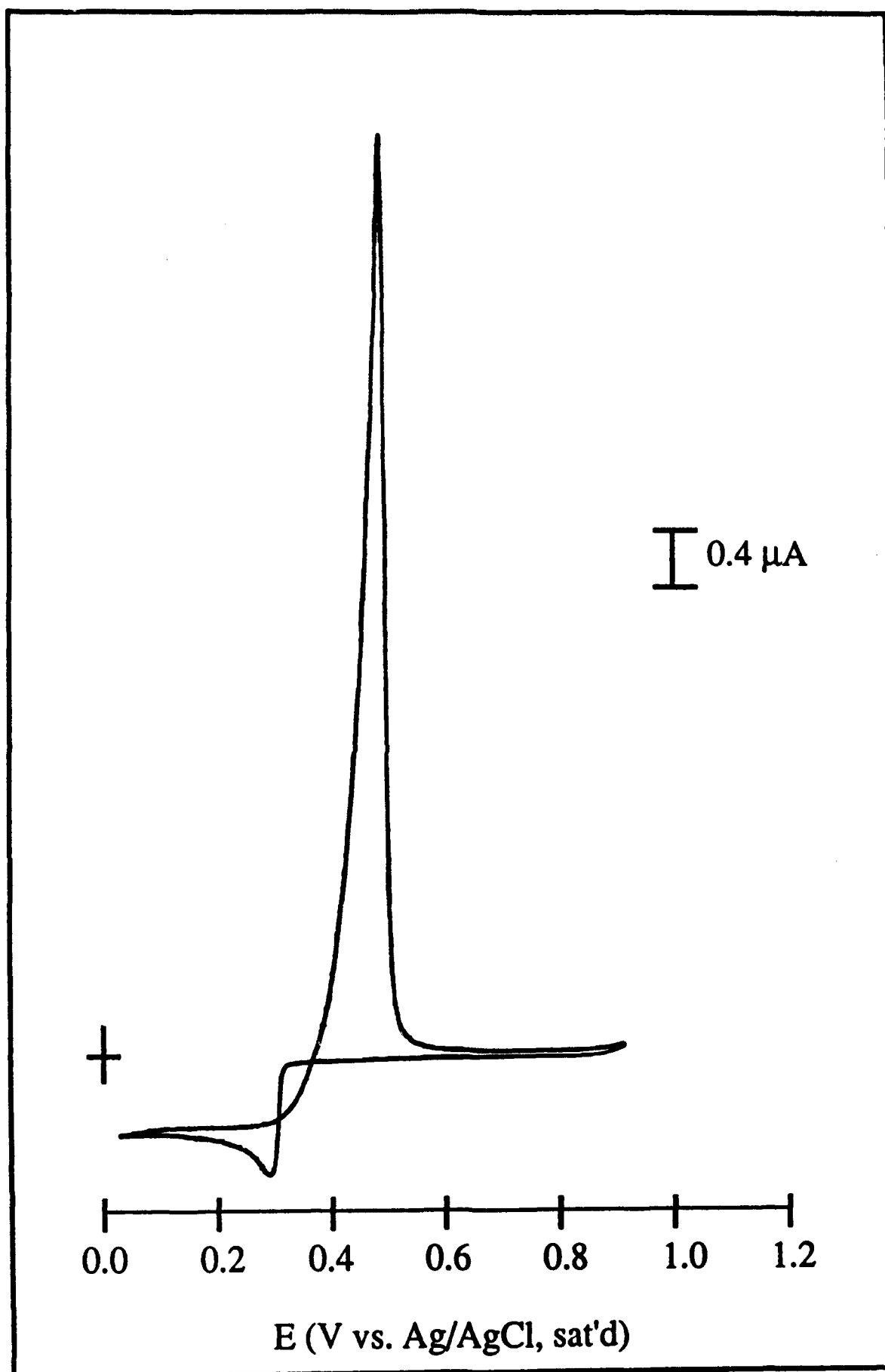


Figure 7B

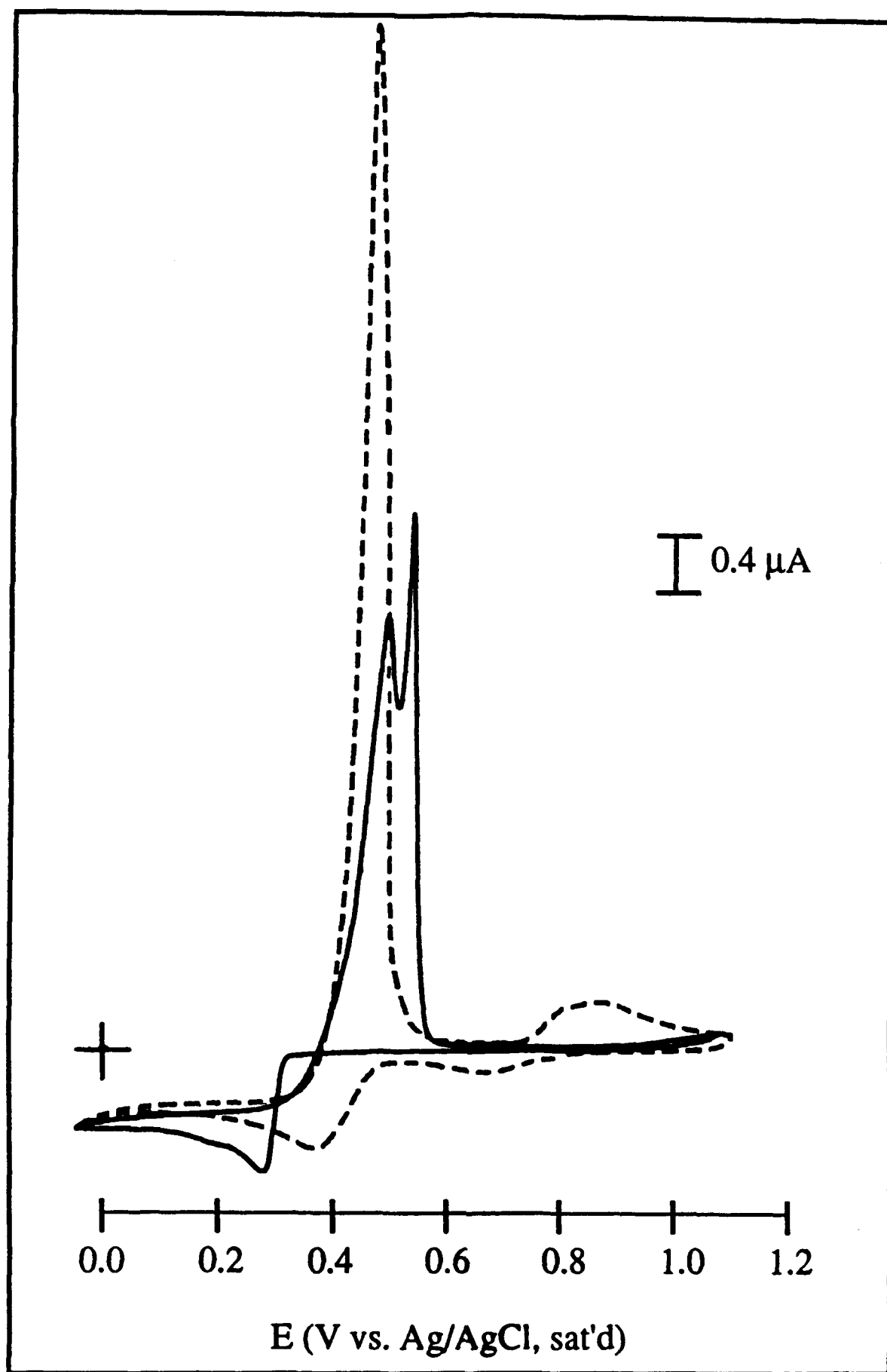


Figure 8A

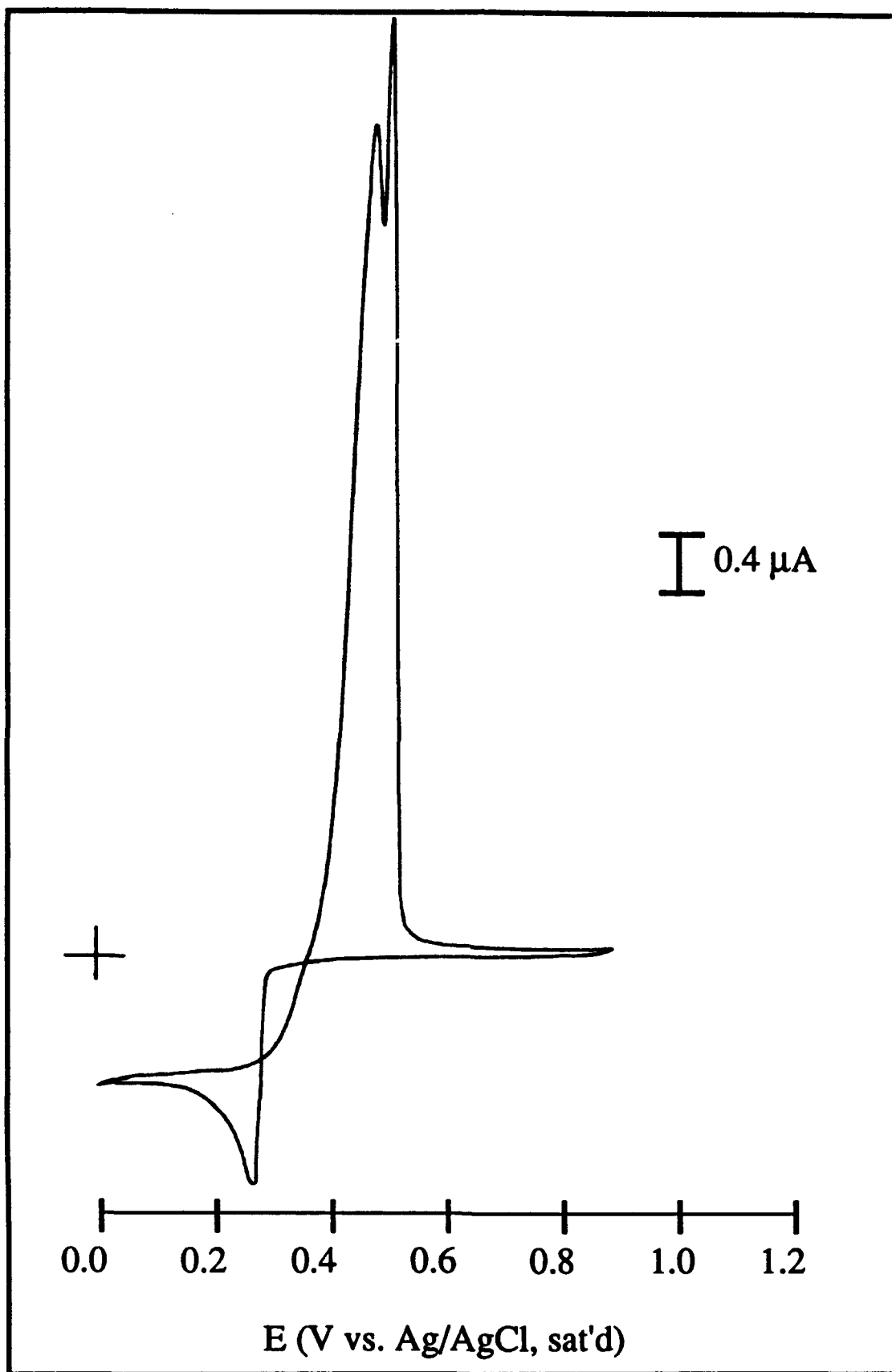


Figure 8B